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A new family of conducting polymers based on the thiophene-phenylene-thiophene repeat unit has been prepared by electrochemical and chemical polymerization routes. Optical band gaps have been correlated with calculated torsional angles. Large scale preparation and study of electroactive polymers and composites, in our ongoing collaboration with General Dynamics, has continued. Copolymers of 3-alkylthiophenes have been prepared. Anion transport in polypyrrole/anthraquinone sulfonate using UV/VIS spectrophotometry, cyclic voltammetry and hydrodynamic voltammetry has been studied.

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Technical Report No. 16

Electronic and Ionic Transport in Polymers

by

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July 24, 1989

Description of Progress

A new family of conducting polymers, based on the thiophene-phenylene-thiophene repeat unit, has been prepared via electrochemical and chemical polymerization routes. Optical gaps have been correlated with calculated torsional angles. The benefit of this system lies in its facile derivatization on the phenyl ring. In addition to the unsubstituted polymer, the $-CH_3$ and $-OCH_3$ substituted polymers have been prepared. Our collaborative research on large scale preparations of electroactive polymers with General Dynamics Inc. has continued. Chemical modification of poly(pyrrole tosylate) and polypyrrole/poly(styrene sulfonate) films has been investigated along with the preparation of polypyrrole/polyurethane composite foams. Soluble copolymers of 3-butylthiophene/3-octylthiophene, 3-methylthiophene/3-octylthiophene and 3-methylthiophene/3-hexylthiophene have been prepared by $FeCl_3$ polymerization and are being studied and evaluated. New polypyrrole/anthraquinone sulfonate polymers have been synthesized. The release of the anion has been monitored via UV/VIS spectrophotometry, cyclic voltammetry and hydrodynamic voltammetry. The quantity and rate of the anion release are dependent on the film thickness and the applied potential. The (open-circuit) anion exchange kinetics of this system has also been quantified. (A10)

Publications

Papers Published

Panchalingam, V. and Reynolds, J. R. "New Vinylidene Fluoride Copolymers: Poly(vinyl acetate-co-vinylidene fluoride)", *J. Polym. Sci., Polym. Lett.* **1989**, *27*, 201-208.

Reynolds, J. R., Jolly, C. A., Krichene, S., Cassoux, P. and Faulman, C. "Poly(metal tetrathiooxalates): A Structural and Charge Transport Study", *Synth. Met.* **1989**, *31*, 109-126.

Jang, G.-W., Tsai, E. W. and Rajeshwar, K. "Charge Storage and Transport in Thermal Ruthenium Oxide Thin Films", *J. Electroanal. Chem.* **1989**, *263*, 383-397.

Basak, S., Ho, Y.-H., Tsai, E.-W. and Rajeshwar, K. "Luminescent Probes of Ion Transport in Polypyrrole: New Strategies for Luminescence Modulation and Assay of Ion Content in Conductive Polymers", *J. Chem. Soc., Chem. Commun.* **1989**, 462-464.

Reynolds, J. R., Baker, C. K., Jolly, C. A., Poropatic, P. A. and Ruiz, J. P. "Electrically Conductive Polymers", in *Conductive Polymers and Plastics*; Margolis, J. M. Ed.; Chapman and Hall: New York, 1989; pp. 1-40.

Papers in Press

Pomerantz, M. and Victor, M. W. "Synthesis and Characterization of a Series of Alternating Copolymers (Oligomers) Containing Organophospha-λ^5-azene Backbone Moieties", *Macromolecules*, in press.

Tsai, E. W., Basak, S., Ruiz, J. P., Reynolds, J. R. and Rajeshwar, K. "Electrochemistry of Some β-Substituted Polythiophenes. Anodic Oxidation, Electrochromism and Electrochemical Deactivation Behavior", *J. Electrochem. Soc.*, in press.

Reynolds, J. R., Hsu, S. G. and Arnott, H. J. "The Effect of Growth Morphology on the Electrochemical Response of Poly(3-methylthiophene)", *J. Polym. Sci., Phys. Ed.*, in press.

Shaffer, T. D. and Kramer, M. C. "Cyclization vs. Polymerization in Phase Transfer Catalyzed Polythioetherification", *Makromol. Chem.*, in press.

Shaffer, T. D. and Sheth, K. A. "Mesomorphic Transition Metal N_2O_2 Chelates", *Mol. Cryst. Liq. Cryst.*, in press.

Shaffer, T. D. "PTC Polyetherification Through Nitro Displacement", *J. Polym. Sci., Polym. Lett.*, in press.

Papers Submitted for Publication

Qiu, Y.-J. and Reynolds, J. R. "Poly[3,6-(carbaz-9-yl)propanesulfonate]: A Self-Doped Polymer with Both Cation and Anion Exchange Properties", *J. Electrochem. Soc.*, submitted for publication.

Sharma, S. C., Krishnamoorthy, S., Naidu, S. V., Eom, C. I., Krichene, S. and Reynolds, J. R. "Positron Annihilation and Conductivity Measurements on Poly(pyrrole tosylate) and Poly(pyrrole fluoride)", *Phys. Rev. B.*, submitted for publication.

Basak, S., Nayak, K,. Marynick, D. S. and Rajeshwar, K. "Synthesis, Characterization, Theoretical Modeling, and Polymerization of New Fluorophore-Containing Derivatives of Thiophene and Pyrrole", *Chemistry of Materials*, submitted for publication.

Chien, J. C. W., Martinez, M. R., Reynolds, J. R. and Wnek, G. E. "Proton, Carbon-13, Nitrogen-15 NMR of Poly(acetylenes), Poly(pyrroles) and Poly(anilines)", *Macromolecules*, submitted for publication.

Nayak, K. and Marynick, D. S. "The Interplay Between Geometric and Electronic Structure in Polyisothianaphthene, Polyisonaphthothiophene, Polythieno(3,4-b)pyrazine and Polythieno(3, 4-b)quinoxaline", *Macromolecules*, submitted for publication.

New Major Equipment

A dielectric spectrometer (Polymer Laboratories) was obtained and set-up this quarter, expanding our capabilities in measuring the electrical properties of polymers.

Personnel Change

Timothy D. Shaffer has left to accept a position with the General Electric Company.

Meetings Attended and Papers Presented

Pomerantz, M. and Victor, M. W. "Synthesis and Characterization of a Series of Alternating Copolymers Containing Organophospha-λ^5-azene Backbone Moieties" 197th National Meeting of The American Chemical Society, Dallas, TX, April, 1989.

Reynolds, J. R., Baker, C. K. and Gieselman, M. "Preparation and Characterization of Polyheterocycle Polyelectrolyte Molecular Composites", 197th National Meeting of The American Chemical Society, Dallas, TX, April, 1989.

Rajeshwar, K., Ho, Y.-H., Basak, S. and Tsai, E. W. "In Situ Probes of Ion Transport in Redox Processes", 197th National Meeting of The American Chemical Society, Dallas, TX, April, 1989.

Rajeshwar, K. "In Situ Spectroelectrochemical Probes of Ion Transport in Conducting Polymers and Conducting Oxides", 175th National Meeting of the Electrochemical Society, Los Angeles, CA, May, 1989.

Reynolds, J. R. and Panchalingam, V. "Synthesis and Characterization of Poly(vinyl acetate-co-vinylidene fluoride)", 197th National Meeting of The American Chemical Society, Dallas, TX, April, 1989.

Victor, M. W. and Pomerantz, M. "Preparation and Characterization of Alternating Copolymers Containing Organophosphazene Groups". 22nd Annual Meeting-in-Miniature of the Dallas-Fort Worth Section of The American Chemical Society, Denton, TX, April, 1989.

All P.I.'s, Postdoctoral Associates and Graduate Students working on this contract attended The American Chemical Society National Meeting in Dallas, TX, April, 1989.

J. R. Reynolds attended the U. S. Army, Natick, First International Conference on Non-Linear Optical Polymers, at Natick, MA on June 13-14, 1989.

Visits

Robert Uitz, Postdoctoral Associate, visited Prof. Arthur Epstein's laboratory at Ohio State University on June 7, 1989 to discuss techniques for measuring electrical conductivity and thermoelectric power.

Visitors to UTA

Dr. Ishaq Haider, from Hoechst-Celanese Research Division, visited UTA on June 29 and discussed our ongoing collaborations in the area of fiber spinning.

Professor N. Oyama of the Tokyo Institute of Agriculture and Technology visited UTA in April and discussed polymer electrochemistry research.